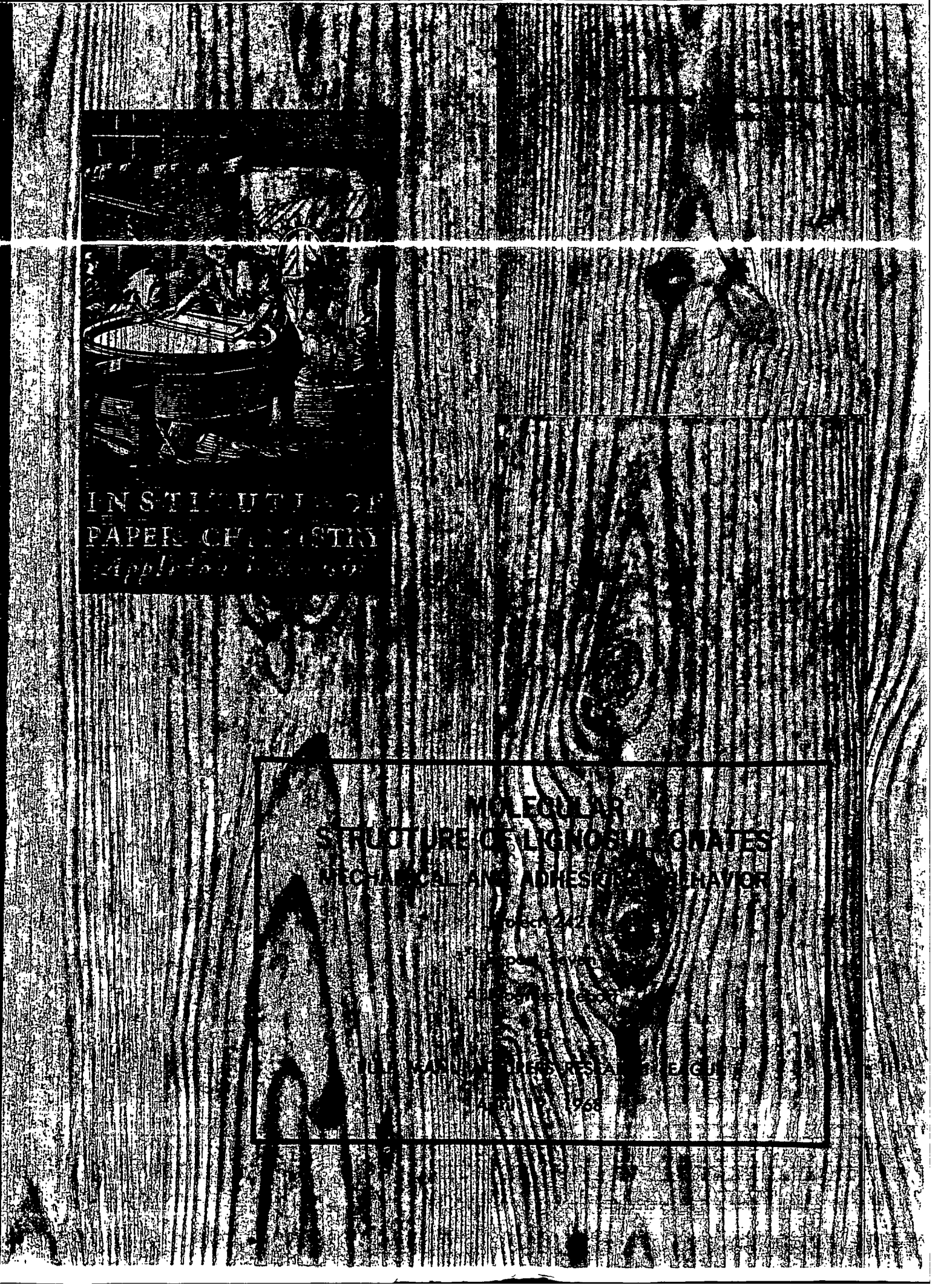
INSTITUTE OF
PAPER CHEMISTRY
Appleton, Wisconsin
MOLECULAR
STRUCTURE OF LIGNOSULFONATES
MECHANICAL AND ADHESIVE BEHAVIOR
Project 2424
Progress Report
April 1968

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

MOLECULAR STRUCTURE OF LIGNOSULFONATES

MECHANICAL AND ADHESIONAL BEHAVIOR

Project 2421

Report Seven

A Progress Report

to

PULP MANUFACTURERS RESEARCH LEAGUE

April 19, 1968

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

MOLECULAR STRUCTURE OF LIGNOSULFONATES

MECHANICAL AND ADHESIONAL BEHAVIOR

SUMMARY

The surface chemical properties of selected lignosulfonates (LSA) have been examined in relation to their utilization as plywood adhesives. Whole liquors and fractions thereof derived from ammonia-base sulfite cooks of a mixed hardwood-softwood furnish were tested for relative viscosity and for surface tension at 73 and 123°F. and these properties were related to the apparent wettability and critical surface tension (γ_c) of southern pine veneer surfaces. The whole liquors included unmodified, ion-exchanged, electrodialyzed, and heat-treated electrodialyzed products. Whole liquors from the same source differed notably in viscosity and to some extent in surface tension. Heat treatment was shown to effect a rapid initial increase in viscosity but had little effect on surface tension at higher concentrations. The viscosity and surface tension of the LSA fractions tended to decrease with decrease in molecular weight with the exception of the lowest molecular weight product which displayed a viscosity close to that of the whole liquor. This fraction is of particular interest since it is the only material showing a surface tension lower than that of the whole liquor and, therefore, it represents the only product capable of wetting a given plywood surface more readily than the whole liquor. However, this product represented only 4.3% of the combined fraction weight.

Exploratory tests with southern pine springwood veneer showed a decrease in the wettability of the surface as a function of aging at room temperature. The critical surface of a veneer surface aged six days was found to be in the order of 32-33 dynes/cm. This value of γ_c is lower than the liquid surface tension of the LSA liquors and, under these conditions, the lignosulfonates would not be expected to function as good adhesives.

INTRODUCTION

This is Progress Report Seven on Project 2421 entitled "Molecular Structure of Lignosulfonates." This aspect of the project is concerned with an investigation of the relationship between lignin structure and its mechanical and adhesional behavior. More specifically, the present report summarizes results obtained to date in measuring the surface chemical properties of lignosulfonates as related to their utilization as plywood adhesives. The viscomechanical properties of lignosulfonates will form the subject matter of the next report.

Recent theories of adhesion and supporting experimental evidence indicate that both the geometric structure and the interfacial composition of the surface play important roles in practical processes such as plywood adhesion. Theoretically, adhesion should occur between any two solid surfaces if the surfaces are made sufficiently smooth and are placed in intimate contact. However, from the practical standpoint, solid surfaces cannot be made sufficiently smooth to yield the necessary molecular contact. In such cases contact is aided with an adhesive which subsequently solidifies. One of the requirements of an adhesive is that it spread on the surface to which it is applied, i.e., it must have a positive spreading coefficient ($\underline{S}$) as expressed in the following equation:

$$S = W_A - W_C \qquad (1)$$

where $\underline{W_A}$ is the work of adhesion and $\underline{W_C}$ is the work of cohesion. $\underline{W_A}$ and $\underline{W_C}$, in turn, are commonly expressed in terms of surface energies or the numerically equivalent surface tension values as follows:

$$W_A = \gamma_S + \gamma_L - \gamma_{SL} \qquad (2)$$

and

$$W_C = 2\gamma_L \qquad (3)$$

where γ_S, γ_L, and γ_{SL} are the surface tensions of the solid-air, liquid-air, and solid-liquid interfaces, respectively. Substitution of Equations (2) and (3) into Equation (1) yields:

$$S = \gamma_S - \gamma_L - \gamma_{SL} \qquad (4)$$

In general, if the intermolecular attractive forces between surface molecules of the adhesive film and the solid are equal to, or greater than, the forces of cohesion between the adhesive molecules themselves, good adhesion should theoretically occur. If separation of film and substrate occurs under this condition, failure usually takes place within one of the components and not at the interface. Introduction of the following relationship

$$\gamma_S - \gamma_{SL} = \gamma_L \cos \theta_A \qquad (5)$$

into Equation (2) under conditions of negligible vapor pressure of the liquid yields

$$W_A = \gamma_L(1 + \cos\theta_A) \qquad (6)$$

where θ_A is the advancing contact angle formed by the liquid on the solid surface at the moment of contact. The contact angle is useful as a means of defining the degree of wettability of the solid and the conditions under which the liquid will spontaneously spread. For example, if θ is greater than zero, the liquid is non-spreading and will only partially wet the solid surface. If θ is zero, the liquid will wet the solid completely and spread at a rate determined by viscosity, surface tension, and surface roughness.

The effect of viscosity on the penetration of a liquid adhesive into a porous substrate is indicated by the idealized equation

$$\ell^2 = \frac{\gamma_L r t \cos\theta}{2\eta} \qquad (7)$$

where ℓ is the distance penetrated in time t, γ_L is the surface tension of the adhesive, r is an average pore diameter, θ is the contact angle, and η is the viscosity of the adhesive. Differentiation of Equation (7) with respect to time yields the corresponding rate of penetration equation:

$$\frac{d\ell}{dt} = \frac{\gamma_L r \cos\theta}{4\eta\ell} \qquad (8)$$

Equation (8) is valid only when the contact angle is acute, when laminar flow exists, and when air resistance, gravitational, and inertial effects may be excluded or neglected.

The effect of surface roughness on contact angle is indicated by a modification of Equation (5) as follows:

$$\text{Cos } \theta_{AA} = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \sigma_1 = \sigma_1 \cos \theta_A \qquad (9)$$

where θ_{AA} is the apparent advancing contact angle and σ_1 is a roughness factor equal to the ratio of the actual surface area to the geometric surface area. When the solid surface is rough, Equation (9) predicts that θ_{AA} will be greater than θ_A if θ_A is obtuse, and θ_{AA} will be less than θ_A if θ_A is acute. In other words, roughness of the solid surface magnifies the wetting or nonwetting property of the surface depending upon the magnitude of the real contact angle θ. For composite heterogeneous surfaces, Equation (9) may be further modified to yield

$$\text{Cos } \theta_{AA} = \sigma_1 \text{ Cos } \theta_A - \sigma_2 \qquad (10)$$

where, for fibrous structures, σ_1 becomes the solid fiber surface area and σ_2

represents the area of air spaces per unit geometric area. Equation (10) shows that, whereas the roughness factor σ_1 may either increase or decrease θ_{AA}, depending upon whether θ_A is obtuse or acute, the porosity factor σ_2 always increases θ_{AA}. Due to the porosity factor, it is possible to have an obtuse apparent advancing contact angle when the real advancing contact angle is acute.

The work of adhesion was previously defined in terms of surface tension and contact angle [Equations (2) and (6)]. In the case of an organic liquid spreading on an organic solid surface it is reasonable to assume that γ_{SL} is negligibly small in comparison with γ_L and, hence,

$$W_A = \gamma_S + \gamma_L \qquad (11)$$

While the absolute surface tension of a solid is difficult to determine with accuracy, a useful approximation (critical surface tension, γ_C) can be determined according to a method described by Shafrin and Zisman (1). The critical surface tension is defined by the intercept of a straight-line plot of $\text{Cos}\theta_A$ vs. γ_L with the $\text{Cos}\theta_A = 1$ axis. According to theory, the surface tension of the liquid adhesive must be equal to or less than the critical surface tension of the solid in order for spreading and adhesion to occur. In determining γ_C, measurements are made of the contact angles formed by appropriate liquids of known surface tension on a given solid surface. The choice of liquids for this purpose would, of course, be governed by lack of solvency, interaction, and other effects. Zisman and others (2,3) have found this concept useful in describing the spreading and adhesive behavior of liquids on a variety of solid surfaces.

Fowkes (4) proposes a means of determining the dispersion force contribution to the surface tension of a solid by means of the following equation

$$\text{Cos}\theta_A = -1 + 2\sqrt{\gamma_S^d} \cdot \sqrt{\gamma_L^d/\gamma_L} \qquad (12)$$

where $\gamma_{\underline{S}}^{\underline{d}}$ and $\gamma_{\underline{L}}^{\underline{d}}$ are the dispersion force contributions to the solid and liquid surface tensions, respectively. Since only dispersion forces are prevalent in many low energy solid surfaces, $\gamma_{\underline{S}}^{\underline{d}}$ becomes equal to $\gamma_{\underline{S}}$. If $\text{Cos}\theta_{\underline{A}}$ is plotted as a function of $\sqrt{\gamma_{\underline{L}}^{\underline{d}}/\gamma_{\underline{L}}}$, the experimental points should fall on a straight line with an origin of -1 and a slope of $2\sqrt{\gamma_{\underline{S}}^{\underline{d}}}$. Graphing in this manner permits the determination of $\gamma_{\underline{S}}^{\underline{d}}$ from a single contact angle of a hydrocarbon on a low energy surface. Hence, Fowkes' method presents a second possible means of determining the surface tension of certain solids.

EXPERIMENTAL

LIGNOSULFONATE SAMPLES FOR SURFACE CHEMICAL STUDIES

Initial studies concerned with the adhesional behavior of lignosulfonates (LSA) were directed at surface tension and viscosity measurements. Samples of ammonia-base spent sulfite liquor from a mixed hardwood-softwood furnish were provided by PMRL for examination. Included among these were an ion-exchange whole liquor, an electrodialyzed whole liquor, a heat-treated whole liquor, and two series of fractions from the same whole liquor. A general description of these materials is given in Table I. Transmission-time curves for the fractions which were obtained by Sephadex gel permeation are given in Fig. 1 and 2.

Samples 2421-1 through 2421-3C were supplied as approximately 40% solutions and were diluted with distilled water to provide lower concentrations. Efforts were made to dissolve the first series of fractions (2421-4 and 5 through 2421-16-20) at 40% solids but only Samples 2421-12 and -13 proved to be completely soluble. The lower molecular weight fractions in that series (2421-14 through 2421-16-20) contained a trace of insoluble material, whereas the higher molecular weight fractions were found to contain substantial amounts of insoluble matter. The latter materials resisted solution upon dilution to 5% solids and after extended stirring at room temperature or slightly above.

The second series of fractions (2421-3-1 through 2421-3-9-12) was taken to dryness by freeze-drying which provided for much improved water solubility. These materials were readily dissolved at 40% solids for subsequent viscosity and surface tension measurements.

TABLE I

LSA SAMPLES FOR SURFACE CHEMICAL STUDIES

Sample Code No.	Description	Approximate Amount Available
2421-1	Whole liquor, No. 67-36 R2	100 ml.; 39.1% solids
2421-2	Sample 2421-1, ion exchanged	50 ml.; 40% solids
2421-3	Whole liquor, No. 66-2; Run 38, electrodialyzed	150 ml.; 40% solids
2421-3A	Sample 2421-3, heat-treated 5 min. at 230°F.	4 ml.; 40% solids
2421-3B	Sample 2421-3, heat-treated 15 min. at 230°F.	4 ml.; 40% solids
2421-3C	Sample 2421-3, heat-treated 60 min. at 230°F.	4 ml.; 40% solids
2421-4 & 5	Fractions of Sample 2421-3; all fractions were taken to dryness under vacuum at approximately 75°C.; in general, the molecular weight of the fractions decreases with increase in sample number	1 g.
2421-6 & 7		1 g.
2421-8		1 g.
2421-9		1 g.
2421-10		1 g.
2421-11		1 g.
2421-12		1 g.
2421-13		1 g.
2421-14		1 g.
2421-15		1 g.
2421-16-20		1 g.
2421-3-1	Fractions of Sample 2421-3; all fractions taken to dryness by freeze-drying; in general, the molecular weight of the fractions decreases with increase in sample number	1.7 g.
2421-3-2		1.2 g.
2421-3-3		2.7 g.
2421-3-4		1.5 g.
2421-3-5 & 6		1.4 g.
2421-3-7		3.3 g.
2421-3-8		1.8 g.
2421-3-9-12		0.6 g.

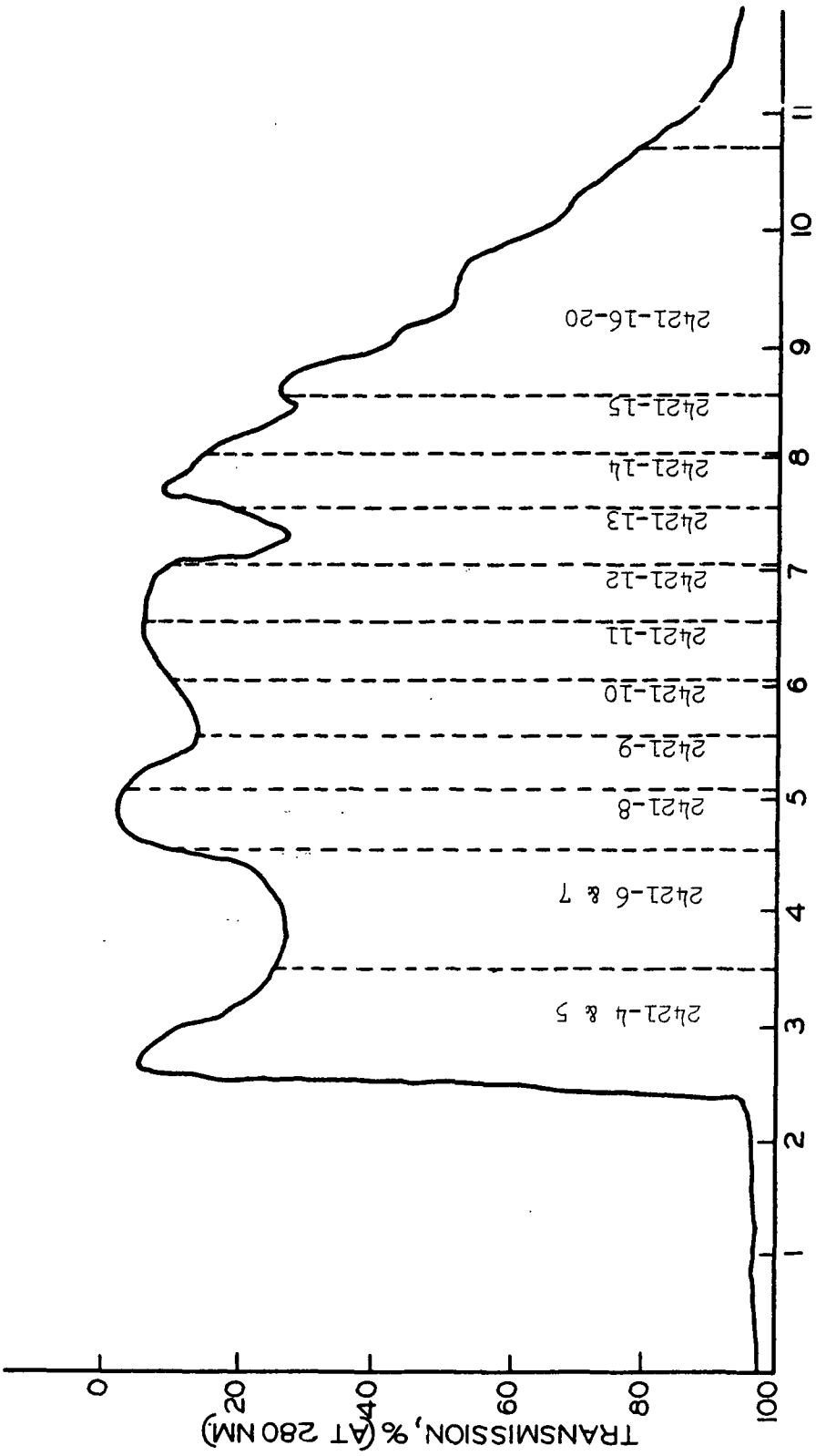

Figure 1. Transmission-Time Relationship for First Series of Lignosulfonate Fractions

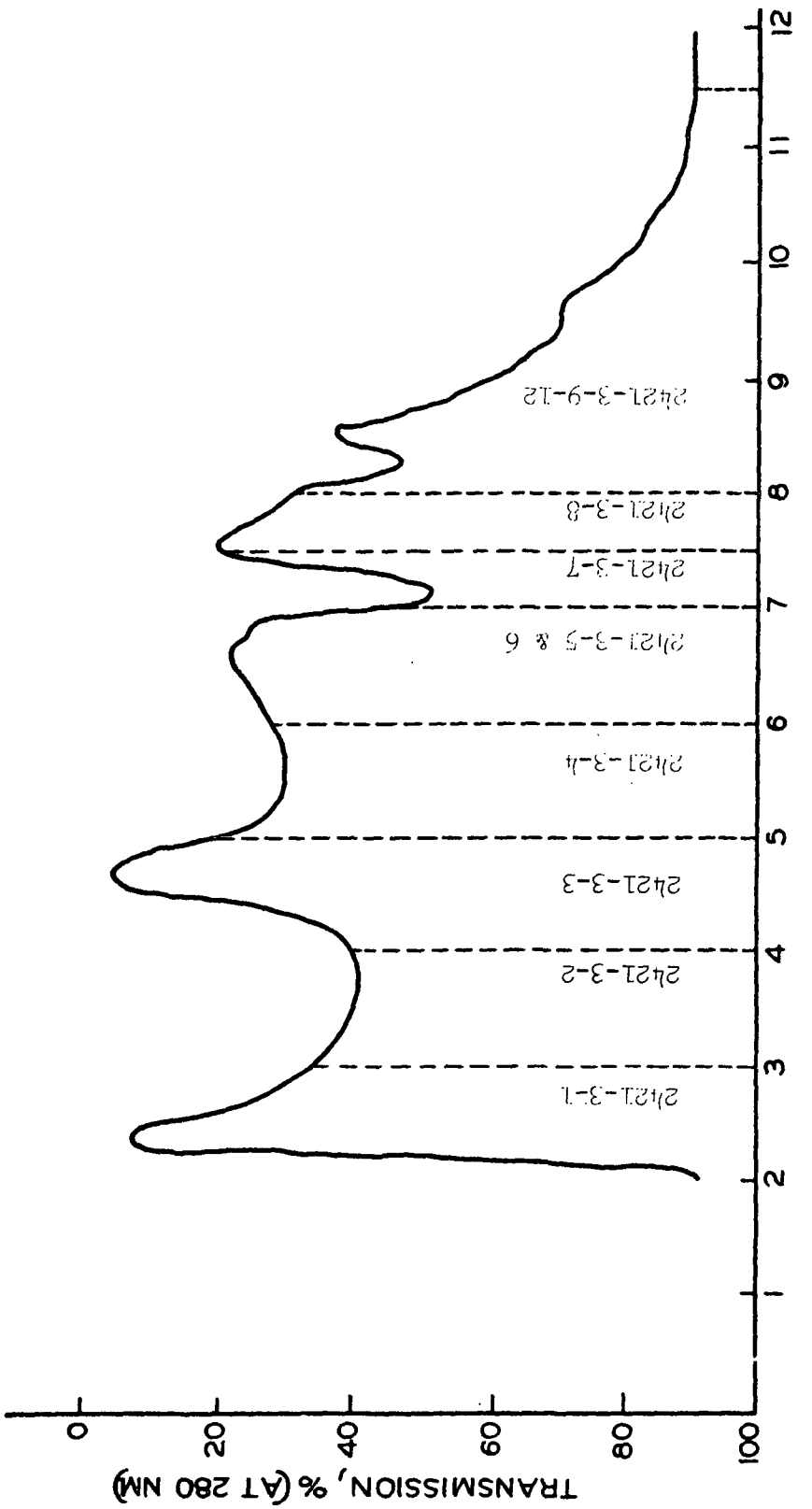

Figure 2. Transmission-Time Relationship for Second Series of Lignosulfonate Fractions

VISCOSITY AND SURFACE TENSION MEASUREMENTS

The relative viscosity of the soluble LSA samples was measured at 123° and/or 73°F. with a Ubbelohde viscometer at concentrations ranging from 5 to 40%. This type of viscometer permits the use of volumes as low as 2 ml. and can thereby accommodate the small volumes associated with solution of the LSA fractions at 40% solids. It was initially planned to dilute the 40% LSA solutions to 10% directly in the viscometer and then remove a portion for surface tension measurements assuming that surface tension would be essentially constant at concentrations in excess of 10%. In working with the fractions, however, it was found that surface tension had not necessarily reached a constant level at 10% solids, hence it was necessary to remove samples from the viscometer at 20% solids for surface tension measurements. A measured portion of the 20% liquor was then returned to the viscometer for further dilution and viscosity determinations.

Viscosity data are recorded in Table II. The relative viscosity of the whole liquors as a function of concentration is shown in Fig. 3. Similar plots for the electrodialyzed liquor and fractions thereof are presented in Fig. 4 and 5. Relative viscosity as a function of the time of heat treatment at 230°F. is shown in Fig. 6.

Surface tension was measured on all LSA samples at 123° and/or 73°F. with a calibrated du Nouy Interfacial Tensiometer. The readings were adjusted for Harkins-Jordan correction factors (5). Routine measurements were made on freshly generated surfaces and spot-check readings were made after the surfaces had aged 10 minutes. Since only minor differences (generally less than 1 dyne/cm.) were encountered as a function of aging of the surface, the initial readings were considered the equilibrium values and only these were recorded in the tables.

TABLE II

RELATIVE VISCOSITY OF LSA SAMPLES AND FRACTIONS

Sample No.	Relative Viscosity (Flow Time), sec. at 73°F. At Concentrations, %					
	40	35	30	20	10	5
2421-1	730	444	281	142	86	69
2421-2	681	435	263	145	86	71
2421-3	1270	768	411	176	95	77
2421-3A	1885	875	469	180	94	75
2421-3B	1905	915	475	186	96	75
2421-3C	2013	965	486	191	96	73
2421-12	--	714	328	150	88	70
2421-13	807	432	292	159	87	70
2421-14	692	536	350	162	88	68
2421-15	762	455	302	149	88	72
2421-16-20	906	--	342	153	88	68
2421-3-1	--	--	--	--	750	295
2421-3-2	--	--	--	--	287	133
2421-3-3	--	--	3246	296	119	84
2421-3-4	--	--	791	220	103	77
2421-3-5 & 6	413	300	223	136	80	68
2421-3-7	288	232	178	118	80	68
2421-3-8	307	237	184	113	78	66
2421-3-9-12	963	541	357	165	99	72
			At 123°F.			
2421-1	497	297	187	91	52	41
2421-2	378	248	164	84	50	41
2421-3	590	--	213	102	55	42
2421-3C	729	384	234	99	54	42
2421-3-3	--	--	601	168	68	50
2421-3-5 & 6	206	156	109	72	45	38
2421-3-8	159	128	95	60	43	37
2421-3-9-12	335	229	167	87	48	39

Viscometer water constants: 58.0 sec. at 73°F.
33.3 sec. at 123°F.

NOTE: The above values represent the average of two determinations.

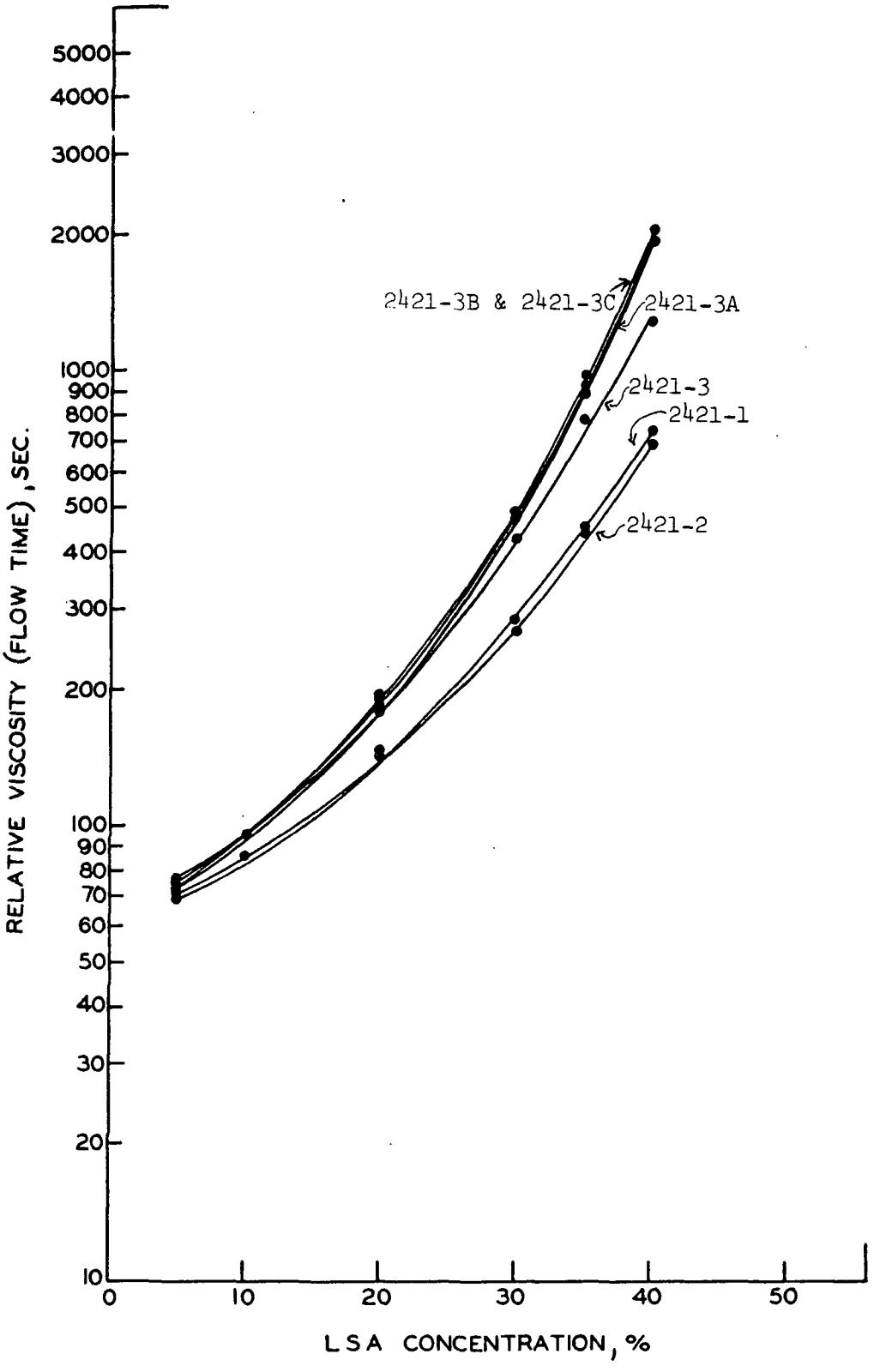

Figure 3. The Relative Viscosity of LSA Samples (Whole Liquors) at 73°F.

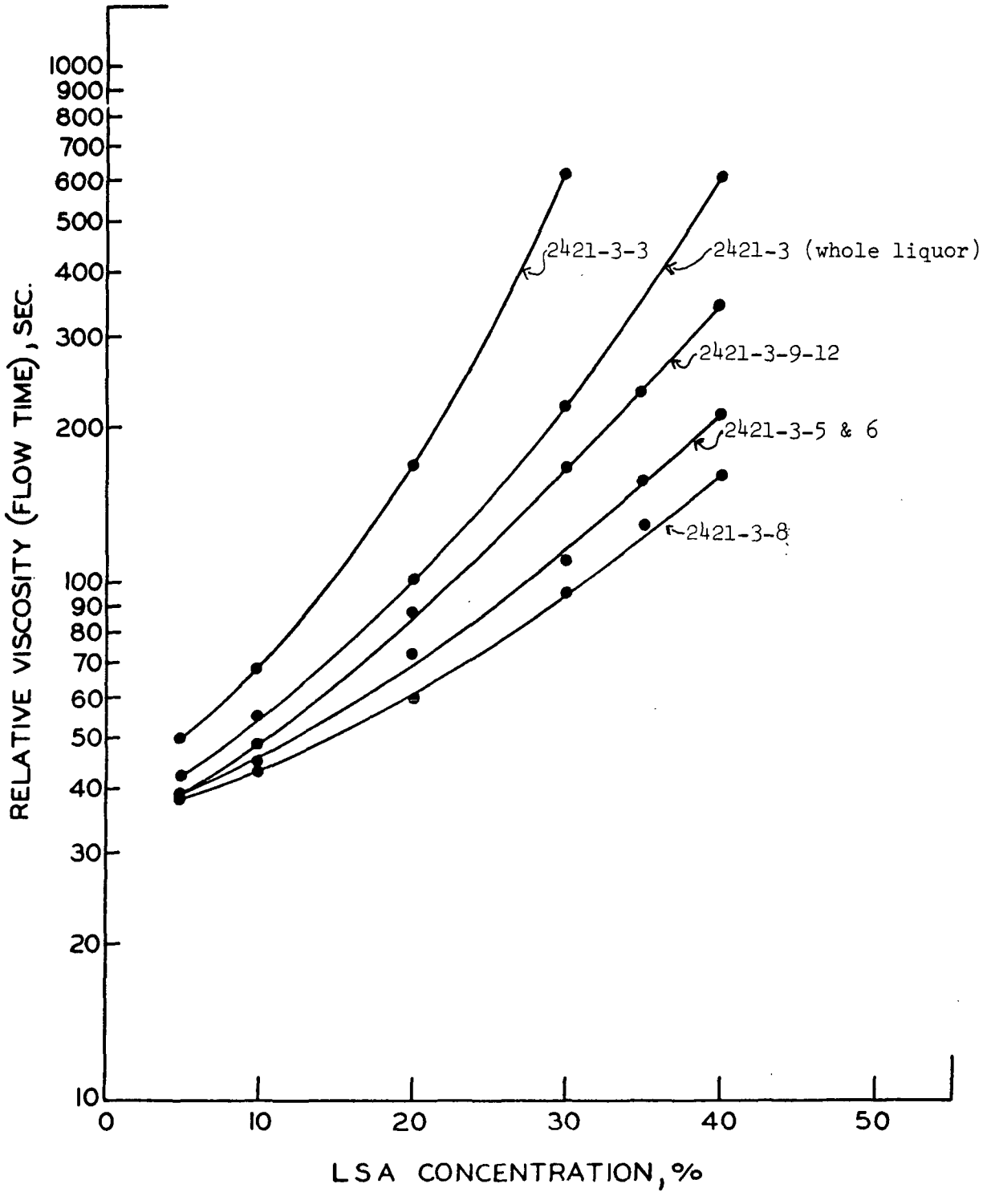

Figure 5. The Relative Viscosity of LSA Fractions at 123°F.

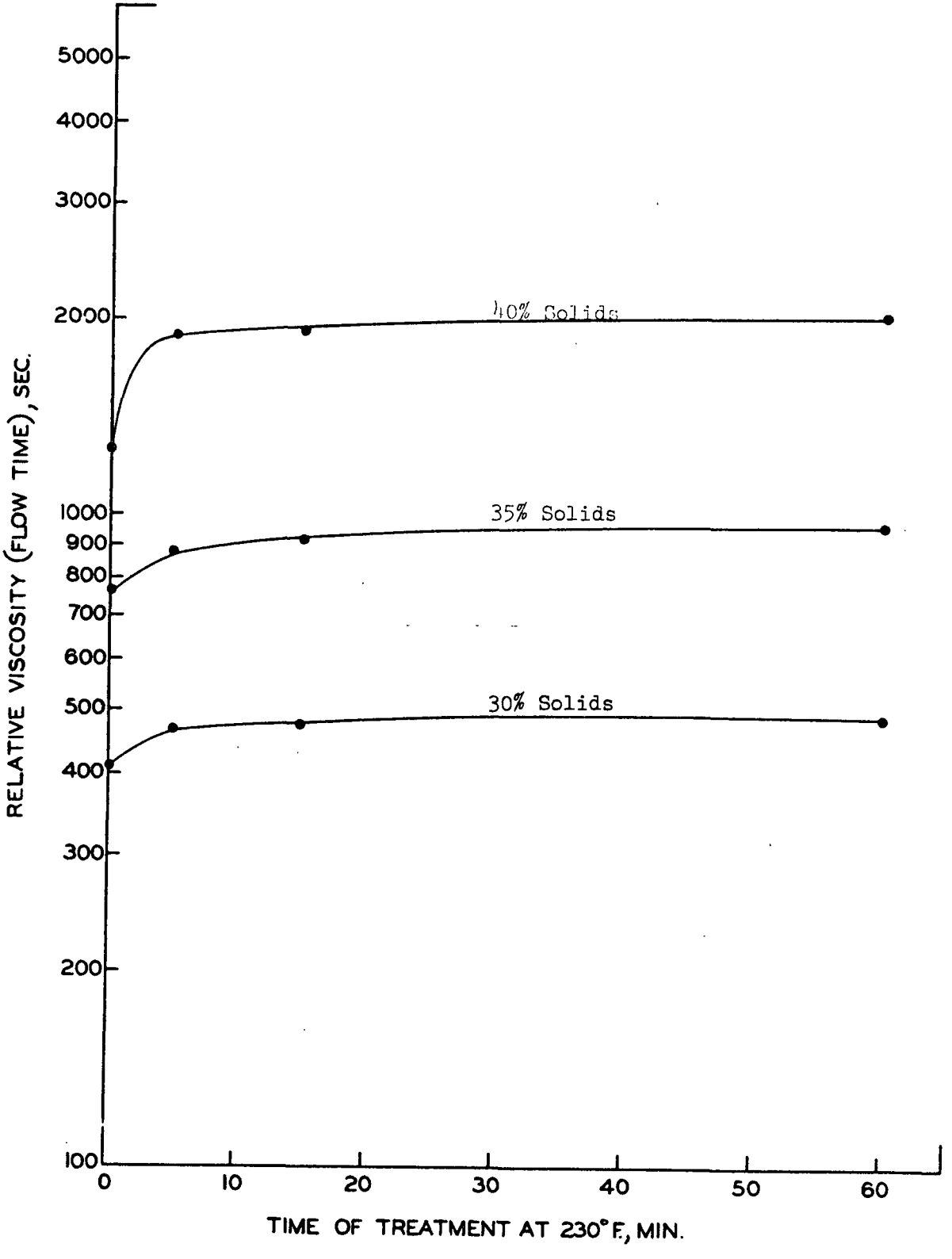

Figure 6. The Effect of Heat Treatment on the Relative Viscosity of LSA Whole Liquor (2421-3)

Surface tension values for the soluble LSA samples are given in Table III; readings for the first series of fractions are presented in Table IV. Surface tension-concentration relationships for the whole liquors are shown graphically in Fig. 7. Surface tension-concentration relationships at 73 and 123°F. are presented in Fig. 8 and 9.

TABLE III

SURFACE TENSION OF SOLUBLE LSA SAMPLES AND FRACTIONS

	Surface Tension, dynes/cm. (corrected) at 73°F. At Concentrations, %									
Sample No.	40	35	30	20	10	5	2	1.0	0.5	0.25
2421-1	40.8[a]	41.4	40.6	40.3	40.6	41.0	42.3	43.5	44.0	45.7
2421-2	41.6	42.0	41.8	42.1	41.0	40.7	43.9	44.7	48.7	51.5
2421-3	43.6	43.9	44.3	44.1	43.1	44.2	44.2	46.8	48.6	50.9
2421-3A	--	--	--	44.3	45.1	45.6	--	--	--	--
2421-3B	--	--	--	43.3	45.6	47.9	--	--	--	--
2421-3C	--	--	--	45.1	45.1	47.7	--	--	--	--
2421-3-1	--	--	--	53.0	52.5	52.8	--	--	--	--
2421-3-2	--	--	--	50.8	51.3	52.0	--	--	--	--
2421-3-3	--	--	--	50.0	51.5	52.0	--	--	--	--
2421-3-4	--	--	--	48.5	49.2	51.4	--	--	--	--
2421-3-5 & 6	--	--	--	47.9	47.6	49.1	--	--	--	--
2421-3-7	--	--	--	49.2	50.4	52.6	--	--	--	--
2421-3-8	--	--	--	47.2	47.1	50.9	--	--	--	--
2421-3-9-12	--	--	--	38.1	39.1	40.0	--	--	--	--
	At 123°F.									
2421-1	39.8	38.3	38.2	38.3	38.1	38.2	39.7	40.5	41.9	43.9
2421-2	40.2	39.3	39.5	38.5	38.6	39.1	41.5	42.9	43.4	46.4
2421-3	--	--	--	39.9	40.4	42.3	--	--	--	--
2421-3C	--	--	--	39.2	38.4	42.2	--	--	--	--
2421-3-3	--	--	--	46.4	46.2	46.1	--	--	--	--
2421-3-5 & 6	--	--	--	43.2	44.4	44.2	--	--	--	--
2421-3-8	--	--	--	43.2	42.8	42.7	--	--	--	--
2421-3-9-12	--	--	--	33.7	33.7	34.3	--	--	--	--

[a] Surface tension at 39.1% solids.

NOTE: The above values represent the average of three determinations.

TABLE IV

SURFACE TENSION OF LSA FRACTIONS 2421-4 & 5 THROUGH 2421-16-20

Sample No.	Surface Tension, dynes/cm. (corrected) at 73°F. At Concentrations, %		
	20	10	5
2421-4 & 5	--	46.4	50.7
2421-6 & 7	--	52.3	52.4
2421-8	--	52.8	55.1
2421-9	--	54.2	54.1
2421-10	--	51.9	53.1
2421-11	--	52.5	52.3
2421-12	--	45.6	51.7
2421-13	--	47.4	54.2
2421-14	52.4	53.0	53.7
2421-15	49.6	49.6	51.2
2421-16-20	41.9	41.6	42.2

NOTE: The above values represent the average of three determinations.

SURFACE CHEMICAL PROPERTIES OF PLYWOOD VENEER

Exploratory experiments were carried out to show the effects of surface aging on the wettability and critical surface tension (γ_c) of southern pine veneer. Sheets of the veneer were cut into 1/2 x 1-inch sections and fresh, smooth surfaces were prepared from the sections with a clean microtome. The relative wettability of the surfaces was determined as a function of aging at room temperature by measuring the contact angles formed by drops of glycerine. It was originally planned to measure the critical surface tension of fresh and aged surfaces but it was found that the contact angles formed by liquids of known surface tension changed

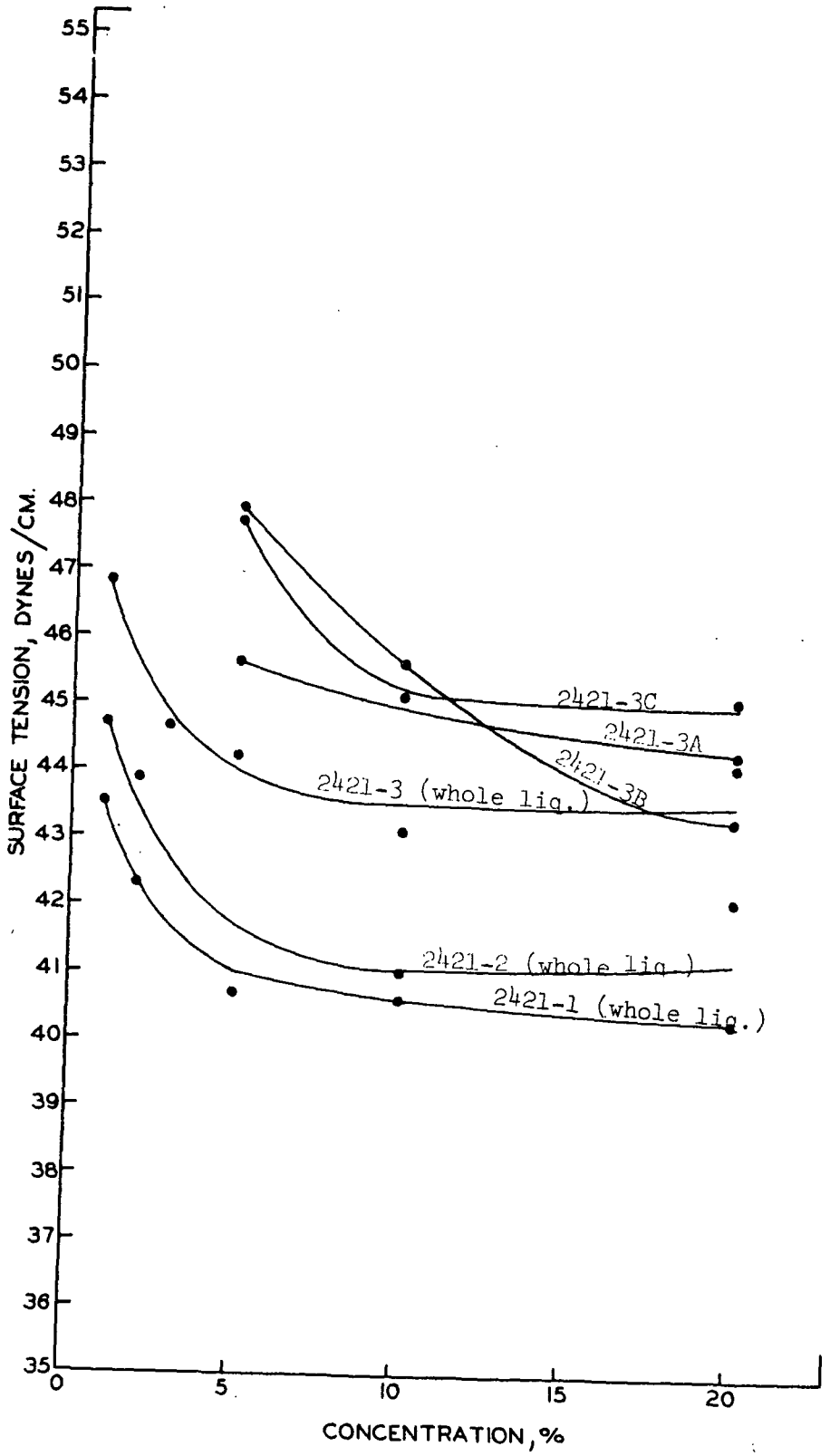

Figure 7. The Surface Tension of LSA Samples (Whole Liquors) at 73°F.

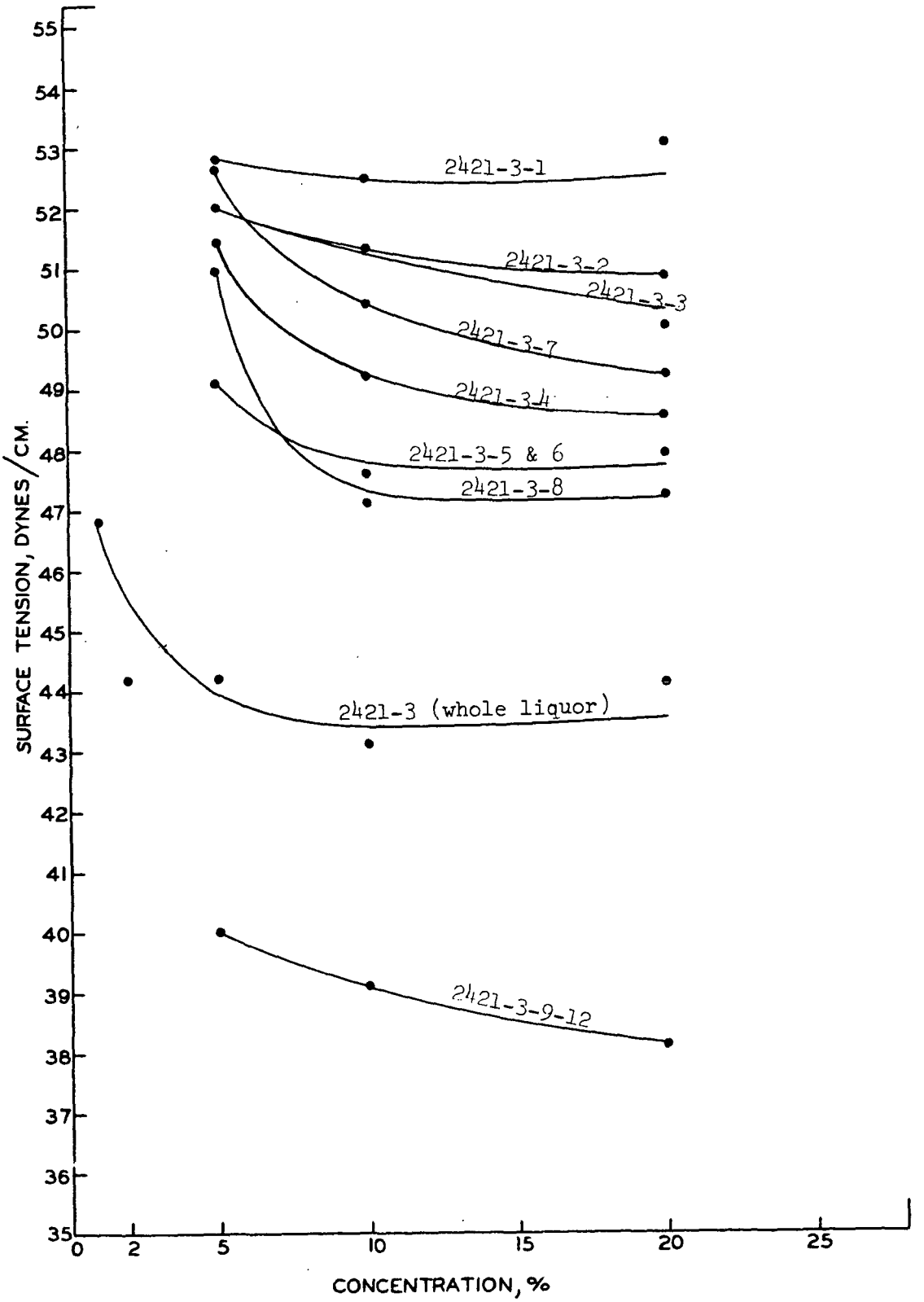

Figure 8. The Surface Tension of LSA Fractions at 73°F.

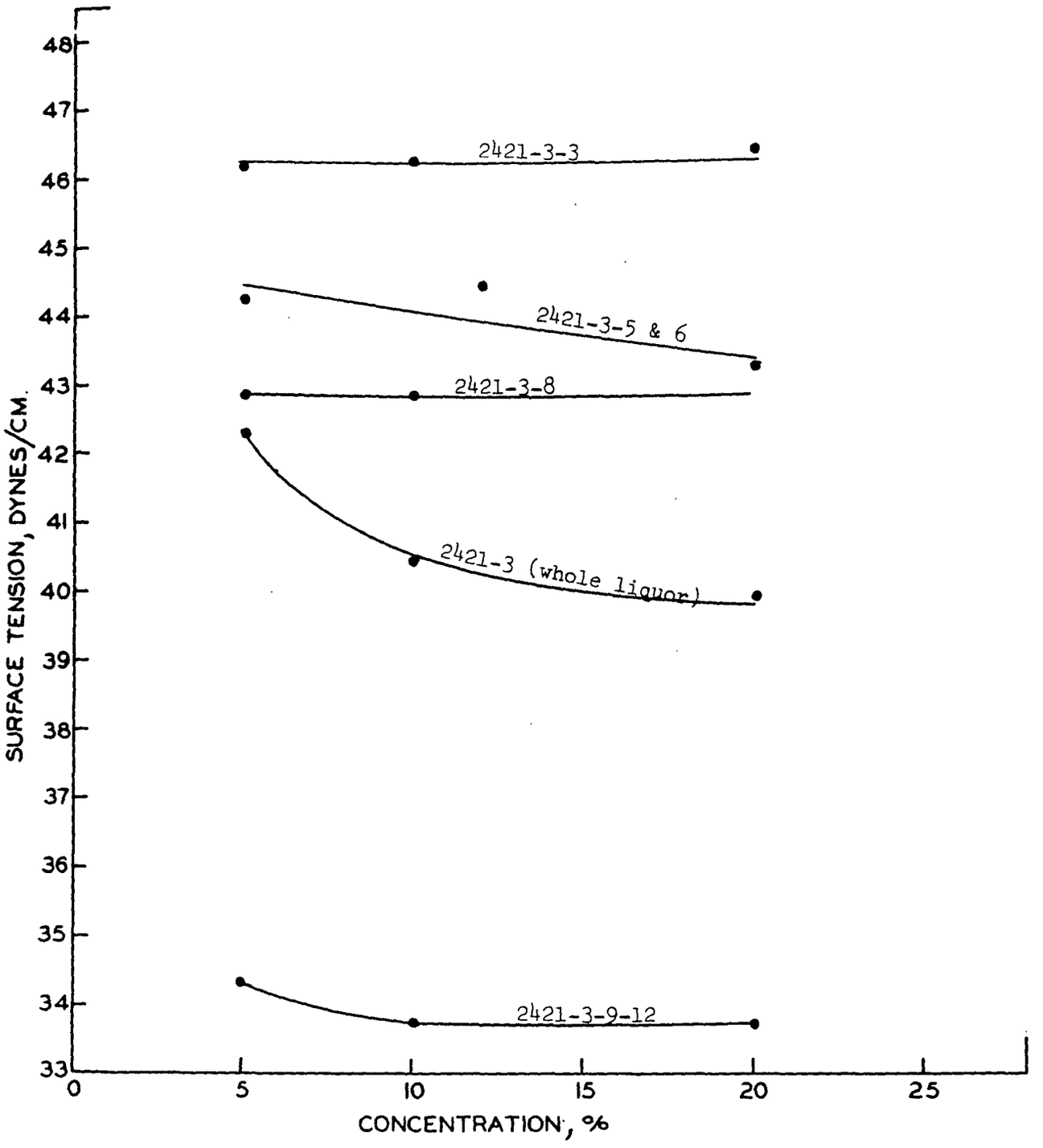

Figure 9. The Surface Tension of LSA Fractions at 123°F.

too rapidly for routine measurement. However, it was found possible to take contact angle measurements with several liquids of relatively high surface tension on surfaces aged six days at room temperature.

Contact angles formed by glycerine and other selected liquids were measured with a direct reading Naval Research Laboratory contact angle goniometer (Model No. A-100, Rame-Hart, Inc.). A drop of known size (6 microliter) was placed on the microtomed surface of veneer and the eyepiece of the goniometer was rotated until the cross-hair formed the tangent to the drop at the point of contact. The contact angle was read directly from a scale graduated in degrees. Readings for critical surface tension were taken within five seconds of contact.

Contact angle data for glycerine on southern pine springwood are recorded in Table V. The change in wettability as a function of aging is shown graphically in Fig. 10. Contact angle data for various liquids on the aged springwood veneer are presented in Table VI and the Cos θ vs. surface tension relationship is shown in Fig. 11.

Note: The contact angle and critical surface tension results recorded in the preceding tables and figures are considered approximate because of the rapid change in angle with time.

TABLE V

CONTACT ANGLE DATE FOR GLYCERINE (γ_L = 63.4 DYNES/CM.)

ON SOUTHERN PINE SPRINGWOOD VENEER

Age of Surface, hr.	Contact Angle θ, degrees	Cos θ
0	36	0.819
4	43	0.731
16	43	0.731
24	45	0.707
40	49	0.656
144	70	0.342

Note: The contact angles listed above represent the average of four readings.

TABLE VI

CONTACT ANGLE DATA FOR VARIOUS LIQUIDS
ON SOUTHERN PINE VENEER

(Springwood, surface aged six days at room temp.)

Liquid	Surface Tension, dynes/cm.	Contact Angle, θ	Cos θ
Distilled water	72.8	107	-0.292
Glycerine	63.4	97	-0.122
1.0% Butanol (in water)	55.0	77	0.225
1.5% Butanol	51.5	70	0.342
2.5% Butanol	46.5	60	0.500

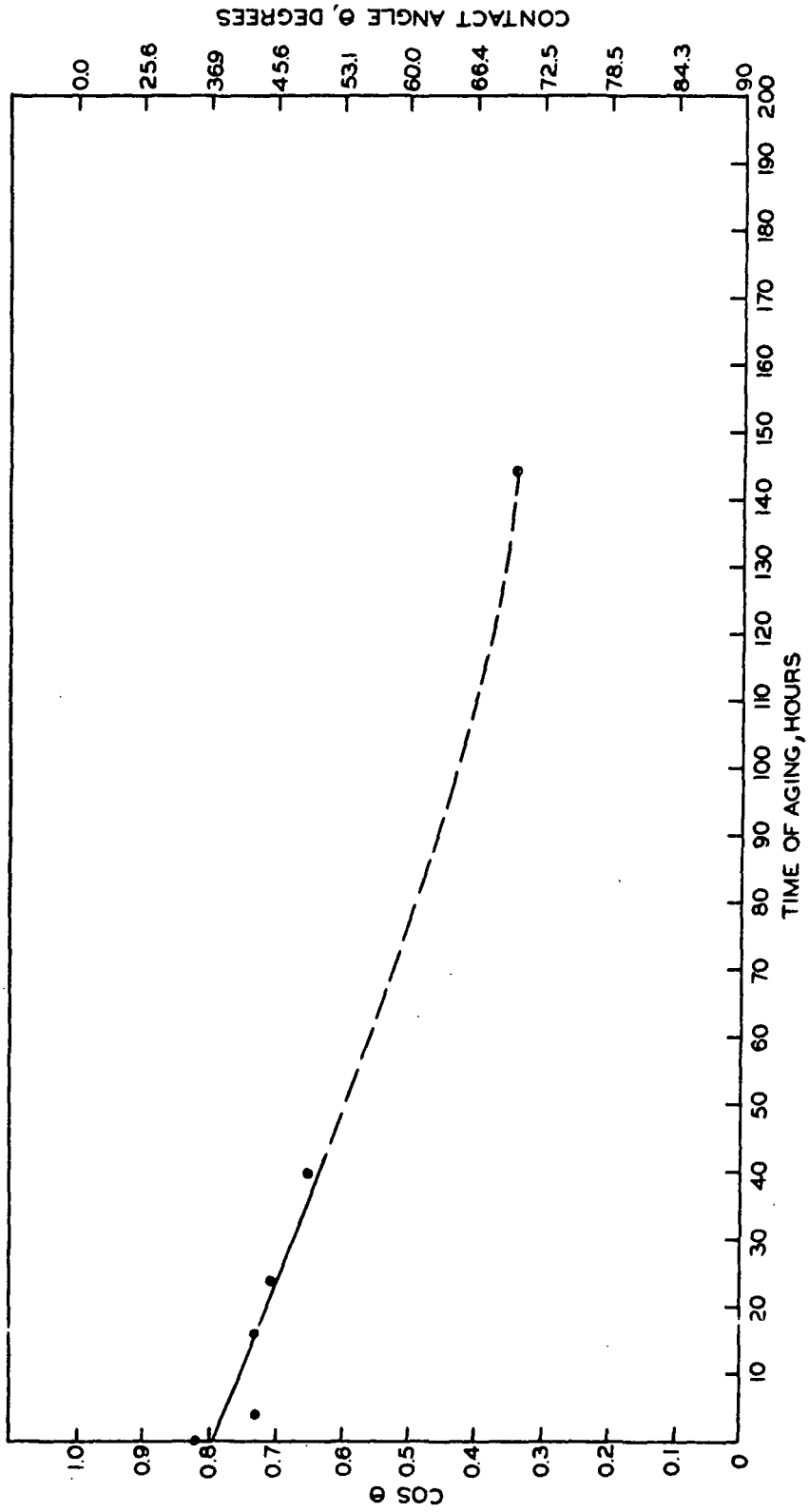

Figure 10. The Effect of Aging on the Wettability by Glycerine of Southern Pine Veneer

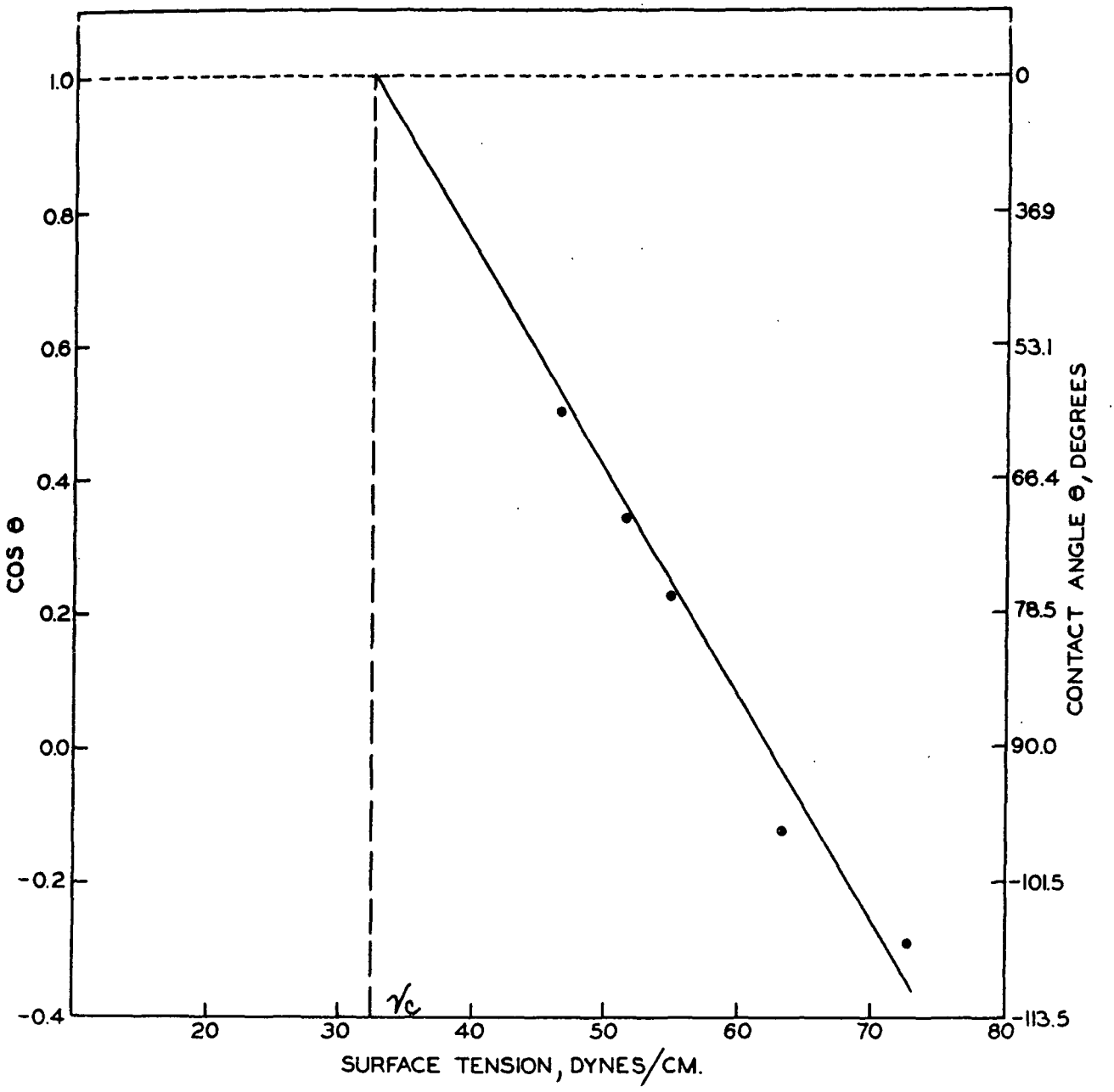

Figure 11. Contact Angle-Surface Tension Relationship for Southern Pine Veneer (Surface Aged Six Days)

DISCUSSION OF RESULTS

Comparisons among the LSA liquors and fractions indicate rather substantial differences in both viscosity and surface tension at concentrations utilized in bonding plywood. The whole liquors differed markedly in viscosity and, to some extent, in surface tension (Tables II and III; Fig. 3 and 7) in spite of the fact that both were of the same type and from the same source. As previously indicated, surface tension and viscosity influence spreadability and penetration, hence variations of this nature in the lignosulfonates would be expected to influence adhesional behavior apart from differences in the surface chemical nature of the plywood panels themselves.

Heat treatment at 230°F. is shown to effect a rather rapid initial increase in viscosity with little change indicated after 5-10 minutes (Fig. 6). Surface tension, on the other hand, does not appear to be materially affected at higher concentrations by heat treatment.

The soluble LSA fractions, with a few exceptions, show a general trend toward decreased viscosity and surface tension with decrease in molecular weight (Fig. 4 and 5, 8 and 9). In so far as viscosity is concerned, the whole liquor assumes an intermediate position which is in keeping with the weight distribution of the fractions. However, the lowest molecular weight fraction (2421-3-9-12) shows somewhat higher viscosity than the immediately preceding fractions and, in fact, its viscosity approaches that of the whole liquor. This particular fraction, which contains strongly adsorbed materials (Fig. 2), displayed markedly lower surface tension than the other products and is the only fraction having a surface tension less than that of the whole liquor. The strong influence of this material on the surface tension of the whole liquor is indicated by the fact that the weight of the fraction represents only 4.3% of the total.

Comparisons at 73° and 123°F. show an expected greater temperature dependence in viscosity than in surface tension. Where direct comparisons can be made, viscosities at 123° ranged from relatively low percentages up to approximately 65% of the values at 73°F. Surface tension, on the other hand, is shown to decrease less than 1 dyne/cm. per 10 degree increase in temperature.

While the surface chemical examination of plywood veneer was very limited in scope, several points of interest are indicated by the results (Tables V and VI, Fig. 10 and 11). Aging of the surface resulted in a decline in wettability which is in keeping with practical plywood bonding experience. The indicated decline in wettability is also in agreement with the results reported by Gray (6) and Herczeg (7) although these investigators found a more rapid decrease than is indicated by the current results. The environment in which the veneer samples were aged would be expected to influence the rate of change in surface properties.

Aging of the veneer surfaces for six days lowered the critical surface tension from some indeterminate level to approximately 32-33 dynes/cm. (Fig. 11). When this value is compared to the liquid surface tension of the whole liquors (Table III, Fig. 7) it becomes apparent that none of the lignosulfonates tested would be theoretically capable of spreading and adhering to the aged surface since, for spreading to occur, the surface tension of the adhesive must be equal to or less than that of the substrate. It is also apparent that, of all products tested, only Fraction 2421-3-9-12 has a surface tension approaching that of the aged plywood surface (Fig. 9). Hence, the advantage or necessity of bonding fresh surfaces is indicated assuming that the liquors utilized in this study were reasonably representative.

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FUTURE WORK

Future work in the adhesional phase of the program will be primarily concerned with further characterization of plywood surfaces. As was mentioned previously, the work completed in this area thus far was exploratory in nature and was limited to one type of wood surface. It is planned to reexamine southern pine veneer surfaces and to extend the study to several other wood surfaces, both springwood and summerwood. In order to avoid, or at least minimize, the problems encountered in measuring initial contact angles on wood surfaces it is planned to photograph the drop at the moment of contact. This procedure will hopefully assist in defining the critical surface tension for freshly generated and moderately aged surfaces. Ultimately, of course, corroborative evidence in the form of practical plywood adhesion tests will be required.

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